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INTEGRATED STUDY OF PHASE COMPOSITION AND STRUCTURE OF POROUS GLASS CERAMICS

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The results of studying the production of porous glass ceramic materials with a permeable structure by the directed crystallization method of a set of phases are presented. The phase composition of materials is studied using x-ray phase, x-ray fluorescence, and electron microscope analysis; microstructural specifics are investigated. The prospects for using materials synthesized as filters for the purification of various media are established.

Use of traditional filtering materials based on paper, coal, and ceramics for media purification in the chemical, food, and medical industries is often limited due to their insufficiently high mechanical strength and thermal and chemical resistance. Glass ceramic porous materials combining the benefits of glass ceramics and filtering ceramics are more reliable.

The authors previously investigated the synthesis of glass ceramics with a permeable structure, which can serve as multiply reusable filters. As a result, a production method was proposed [1, 2] based on the technology of powdered glass ceramics (Scheme 1). The materials used were sand, kaolin, chalk, marble crumb, zinc white, technical magnesium oxide, boric acid, soda ash, and strontium carbonate.

The theoretical basis for synthesis of porous glass ceramics is the method of directed crystallization of glass of a respective chemical composition. The process implies the production of crystalline phases of diopside $CaMgSi_2O_6$ and zinc petalite $ZnAl_2Si_8O_{20}$, which are able to impart high service parameters to materials based on these compounds. The stoichiometry of phases synthesized was taken into account in developing model glasses.

X-ray phase analysis of obtained materials established the presence of such crystalline phases as diopside, gahnite $ZnAl_2O_4$, β-quartz, and another phase (*x*-phase), which is presumably zinc petalite. It should be noted that the presence of the latter in the material is desirable, as zinc petalite has a TCLE of zero and, therefore, can substantially raise the resistance of material to thermal loads. However, it was difficult to identify this compound by x-ray phase analysis, since there are no data on its interplanar distances in the literature. At the same time, it is known that zinc petalite in its structure resembles lithium petalite and, similarly to the latter, is capable of forming solid solutions with β-quartz [3]. Based on these literature data and taking into account the authors' own x-ray diffraction research, which revealed the presence of the *x*-phase with a certain deviation of the values of β-quartz interplanar distances from the standard values, we assume that the *x*-phase is precisely zinc petalite.

To verify the presence of the zinc petalite phase in the synthesized materials, x-ray fluorescence analysis was used as an additional method of analysis. This was implemented employing an original material analyzer called Sprut that has been developed at the Kharkov Polytechnical University and is intended for nonintrusive elemental analysis of materials based on x-ray fluorescence spectra. The instrument is certified by the Gosstandart (State Standard Committee) of Ukraine and is entered into the State Production Register (No. U703–96).

The physical principle of x-ray fluorescence analysis consists in the interaction of the initial x-ray radiation with atoms of the sample radiated, when electrons are pushed out from inner electron shells. Vacancies that arise in this way are filled up by electrons descending from higher levels. In this process, x-ray quanta are emitted with energy E_i equal to the difference between the energy values of respective electron levels; in our case the numerical value of energy is a constant equal to 35 eV. The value E_i is characteristic for the element excited and can be used for qualitative analysis. The quantity of quanta emitted with energy E_i is proportional to the concentration, which makes it possible to obtain information for quantitative analysis. It should be noted as well that x-ray fluorescence analysis is based on decomposition of radiation by elements in vacuum with a range of elements considered from Na(11) to U(92).

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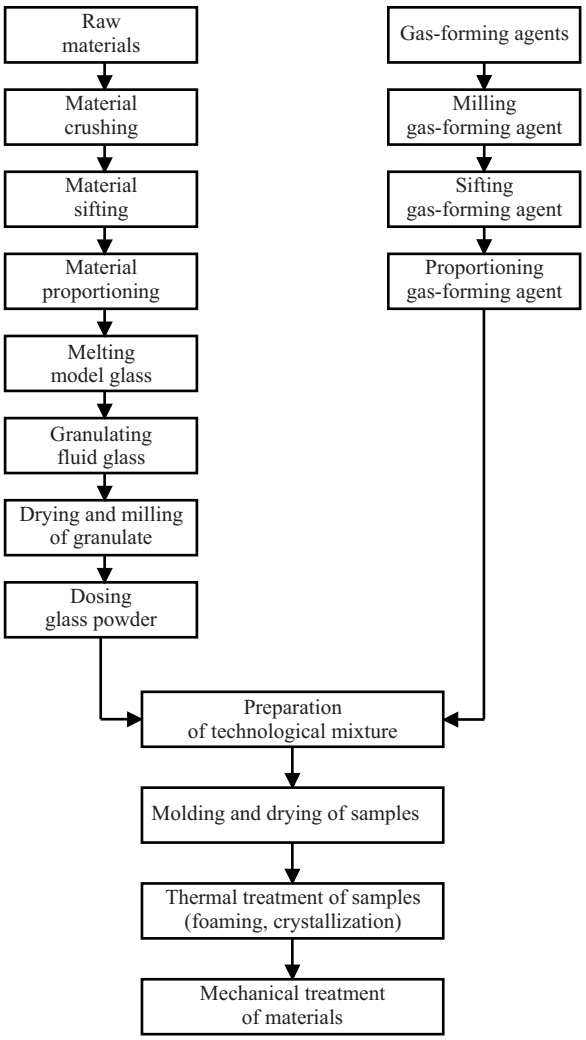
The measurement method implies irradiation of the sample by the x-ray tube spectrum, after which the sample emits fluorescent radiation, which contains sets of quanta with various E_i. Either energy dispersion or resonance reflection from a crystal are used to isolate each of these sets from the total flux. However, instruments based on energy dispersion cannot be accepted for the measurement of polycomponent systems, such as the materials considered, due to their low energy resolution, short linearity range of the recording equipment, and a high background noise level.

In the crystal-diffraction method (resonance reflection from a crystal) two x-ray-optical schemes are used: the Bragg – Soller and the Johanson with a focusing crystal. An important advantage of the Sprut scheme (Bragg – Soller) compared to the classical Johanson scheme is the absence of background noise at small angles of reflection from the analyzer crystals. This background makes it extremely difficult to measure spectral lines with a wavelength of $\leq 8 \times 10^{-11}$ m on standard analyzer crystals and prevents using new x-ray-optical elements with very high reflection coefficients for measuring elements of Period III of the Mendeleev table (Mg, Al, Si, P, S, etc.). The replacement of standard crystals by these new elements made it possible to accelerate 5 – 7 times the count rate of K_α lines for Period III element with a high degree of contrast [4].

To identify the zinc petalite phase, we investigated the intensities of zinc, aluminum, and silicon lines in the materials developed, i.e., the elements comprising the specified phase in the materials obtained. It should be noted that there is a 100% reference standard with the maximum line intensity for each of the elements mentioned. The reference intensity of zinc is 69,000 pulse/sec, that of aluminum is 2800 pulse/sec, and that of silicon 5000 pulse/sec. Table 1 lists the intensities of characteristic lines for Zn, Al, and Si in materials of different compositions with different contents of zinc, aluminum, and silicon oxides.

Based on the data in Table 1, mass contents of zinc, aluminum, and silicon oxides were calculated, which correlated with their quantities in the model glass compositions. Insignificant deviations of the actual content of oxides from the preset value are due to the mutual influence of chemical elements in the implementation of this method. Thus, x-ray fluorescence analysis made it possible to identify the quantitative ratios of zinc, aluminum, and silicon oxides (1 : 1 : 8, respectively), which virtually coincides with the stoichiometry of zinc petalite preset in chemical compositions during their development.

To corroborate the presence of zinc petalite in the materials investigated, their structure was investigated using the direct electron microscopy method (a RÉMMA-101A scanning electron microscope). Figure 1 shows microphotos of synthesized glass ceramics obtained within a temperature interval of 720 – 780°C in fast thermal treatment with and without gas-forming agents.



Scheme 1. Technological scheme for producing porous glass ceramics.

Figure 1*a* – *d* show pore-free crystallized glass PD-45-25, in which individual crystalline formations can be seen at a magnification of × 450 and × 600. X-ray microanalysis made it possible to identify the presence of such elements as Zn, Al, and Si in individual crystals, and judging from the peak intensities on the characteristic spectra, silicon prevails. These data in combination with previous results of x-ray phase analysis may be evidence of the presence of a solid solution based on β-quartz, where the dissolved phase in all probability is zinc petalite.

TABLE 1

Element	Element line intensities in the glass ceramic materials, pulse/sec					
	P-50	P-70	PD-15-35	PD-35-15	PD-25-45	PD-45-25
Zinc	8459	11,854	2539	5920	4237	7618
Aluminum	107	150	32	75	54	97
Silicon	1380	1292	906	991	1226	1311

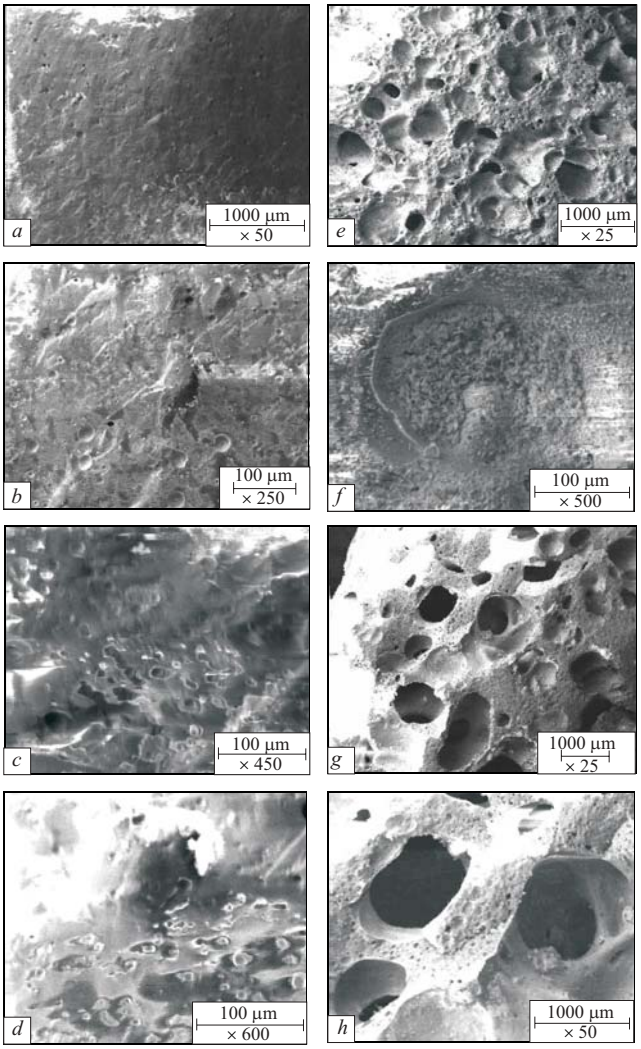


Fig. 1. Electron microscope photos of glass ceramics: *a*, *b*) crystallized model glass PD-45-25; *c*, *d*) new crystalline formation in glass PD-45-25; *e*) surface of porous glass-crystalline material PD-45-25, *f*) surface site of porous glass-ceramic material PD-45-25; *g*, *h*) cross-section of porous glass-ceramic material P-70.

It can be seen from Fig. 1*e* that the surface of synthesized material PD-45-25 has uniform open porosity with pore size ranging from 1×10^{-4} to 7×10^{-4} m. Ample crystallization areas with thin interlayers of the residual vitreous phase are observed in the inter-pore space (Fig. 1*f*), and x-ray microanalysis of the crystallized areas identified as well the presence of microsites containing Zn, Al, and Si.

Glass-ceramic material P-70 (Fig. 1*g*) is uniformly perforated by pores ($d = 10^{-3}$ m), and the interpore partitions ($d = 5 \times 10^{-5}$ m) are also intensely porous. The intercommunicating structure of the pore space is clearly visible (Fig. 1*h*).

A similar complex research using x-ray phase and x-ray fluorescence methods of analysis and electron microscopy was performed on samples of all material listed in Table 1. The results of these studies indicate the presence of a solid solution of β-quartz and zinc petalite in the phase composition of these materials. The microphotos of samples clearly exhibit a structure with uniformly distributed communicating pores, which makes it possible to recommend the developed glass-ceramic materials as filters for purification of various media.

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